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Characterizations of Antimony Tri-Sulfide Chemically Deposited with Silicotungstic Acid

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ABSTRACT

A new chemical deposition method has been developed to prepare photoconducting n-Sb₂S₃ thin polycrystalline films. The solution composition of the deposition bath was 0.025M potassium antimonyl tartarate, 0.4M triethanolamine, 0.025M thioacetamide, and 5×10^{-7} M silicotungstic acid (STA), respectively. The as-deposited and the annealed films were characterized through x-ray diffraction, neutron activation analysis, and the optical absorption investigations. The photoelectrochemical performances of these films were examined. The best photoresponse was observed on the film prepared from a chemical bath containing 5×10^{-7} M STA.

Photoconducting antimony tri-sulfide thin films are generally prepared by vacuum evaporation (1) or by sintering technique (2) using powdered Sb₂S₃ compound as the starting material. This creates the difficulty of achieving the stoichiometric films due to wide differences of the vapor pressures of the constituents at the deposition temperature. Recently there has arisen a sustained effort to produce different chalcogenide thin films by simple and inexpensive chemical deposition methods. Other than Cd-chalcogenides (3, 4), this method is applied to produce good quality, stoichiometric layered semiconductors such as MoS₂ (4, 5) and MoSe₂ (6). The method has also been proven to be the least expensive, low-temperature method, non-polluting, and with an ease for making films of large area of any configuration. Among the different metal sulfides, antimony tri-sulfide finds special applications in vidicon devices (7, 8), microwave devices (9), switching devices (10) and various optoelectronic devices (11).

The activation of electrode surfaces by heteropolyacids (HPAs), e.g., H₄SiW₁₂O₄₀ or H₃PW₁₂O₄₀ has been well established and largely used in the electrocatalysis of the hydrogen evolution reaction at modified semiconductor or metal electrode surfaces (12, 13). The significant improvement of the hydrogen evolution reaction kinetics has also been observed on electrodeposited nickel with various HPAs whereas the electrode fabricated without HPAs do not show any improvement (14, 15). These interesting results have prompted us to examine the effects of incorporating silicotungstic acid (SiW₁₂O₄₀⁴⁻; STA) in the chemical deposition bath of antimony trisulfide thin films.

In this paper we report a new chemical method for the deposition of Sb₂S₃ thin films and their characterizations using x-ray diffraction, neutron activation analysis, optical absorption, resistivity and Hall effect studies, and the photoelectrochemical (PEC) measurements. The pronounced effect of STA with a nominal concentration of 5×10^{-7} M in the chemical deposition bath have been studied along with the effect of annealing.

Experimental Procedure

Thin films of Sb₂S₃ were deposited onto SnO₂-coated glass substrates from an aqueous solution of 0.025M potassium antimonyl tartarate (BDH, AR), 0.4M triethanolamine (BDH, AR), 0.5M ammonia, and 0.025M thioacetamide (BDH, AR) under a magnetic stirrer. Before use, the SnO₂-coated glass slides were cleaned ultrasonically in isopropyl alcohol and dried in pure N₂ atmosphere. The cleaned substrates were then clamped vertically in the plating solution at 300 K. During the Sb₂S₃ film formation, the solution color changed progressively from light to deep yellow and then orange-red at which a thick deposition of Sb₂S₃ films ($\approx 1.0 \mu\text{m}$) were formed on the substrates. After 60 h, the slides were removed and washed thoroughly by water and dried in air. In case of STA-incorporated Sb₂S₃ films, the same procedure was adopted except 5×10^{-7} M STA has been used in the chemical bath. The coated glass slides were then introduced into an oven maintained at 300°C for 1 h in N₂ atmosphere.

The composition and the crystalline status of the as-deposited and the annealed films with and without STA were examined from the powder x-ray diffractograms with a Philips x-ray

diffractometer. The Sb₂S₃ powder was collected by scrapping off the SnO₂-coated glass substrates and used for this study. The chemical composition of the different films was determined from the neutron activation analysis. Optical absorption spectra of the different Sb₂S₃ films deposited on SnO₂ coated glass substrates were recorded from 950 to 540 nm by a Shimadzu UV/VIS spectrophotometer at 300 K. The optical bandgap of the as-deposited and annealed films with and without STA incorporated films were determined from this study.

Resistivity and Hall effect measurements were carried out by four-point probe van der Pauw method. Conducting silver paint was used for electrical contact. The I-V characteristics have been found to be linear within the voltage range of study (20 V) showing the ohmic nature of the contact Sb₂S₃ films. The photoelectrochemical (PEC) measurements were conducted on a standard three-electrode cell geometry. A large-area graphite electrode was used as a counterelectrode. The working redox electrolyte was 0.01M I₂ and 1M KI and degassed thoroughly before and during the experiments. The Sb₂S₃ film surfaces which are not contacted with the electrolyte were covered by microtop lacquer adhesives. The PEC cell was illuminated with a broad band tungsten halogen lamp (Fibre-Lite). The intensity of illumination was calibrated using Oriel solar simulator radio meter (Model 81020).

Results and Discussion

The structural features of the films deposited with and without STA are shown in Fig. 1. The as-deposited film in both the cases, with or without 5×10^{-7} M STA showed a broad x-ray spectrum (Fig. 1a) suggesting that they have an amorphous structure. But the annealed samples (300°C for 1 h, N₂ atmosphere) showed well-defined crystallographic planes (Fig. 1b) and these were identified in the recordings (16). The structural features are consistent with an orthorhombic cell with lattice constants $a_0 = 11.269$, $b_0 = 11.299$, and $c_0 = 3.824$. Figure 1c

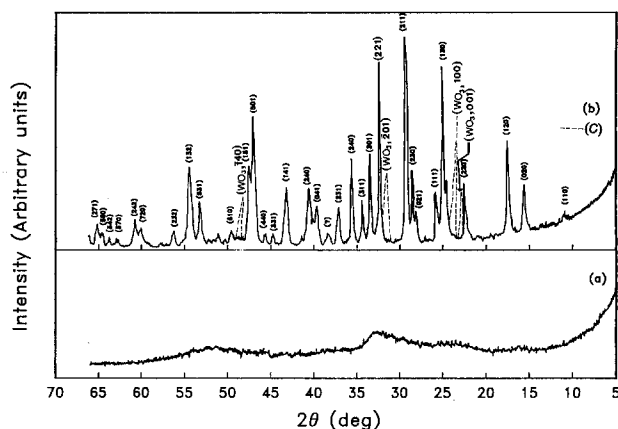


Fig. 1. X-ray diffractogram of an Sb₂S₃ film scrapped off the glass substrates: (a) as deposited film with and without 5×10^{-7} M STA; (b) with annealing at 300°C for 1 h in N₂ atmosphere (without STA) and (c) same as (b) but with 5×10^{-7} M STA.

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Table I. Compositions, electrical properties, and grain sizes of the different films (for the experimental conditions, see the text).

Film	Atomic compositions (%)		Resistivity (ρ , Ω cm)	Carrier concentration (N_d , cm^{-3})	Mobility ($\text{cm}^2/\text{V}\cdot\text{s}$)	Grain sizes (μm)
	Sb	S				
(a) Sb_2S_3 film as-deposited	34.3	65.7	3.8×10^8	—	—	0.12 ± 0.02
(b) Film (a), annealed	36.2	63.8	5.3×10^6	1.2×10^{12}	9.8	0.82 ± 0.1
(c) STA incorporated film, annealed	38.6	61.4	5.0×10^6	2.4×10^{12}	9.2	1.02 ± 0.2

shows the intense peak due to WO_3 , which is incorporated in the Sb_2S_3 film during deposition.

A comparison of the atomic percentage of Sb and S present in the different films are given in Table I. In order to optimize measurement conditions, the powdered sample (scrapped off the substrates) of about 1 mg was irradiated at least three times with the flux of 10^{12} neutrons/ cm^2/s and counted four times with the liquid nitrogen cooled Ge gamma ray detector. The measured accuracy was estimated to be $\pm 5\%$. From the Table I, it is clear that a near-stoichiometric film could only be obtained when the film was prepared from a chemical bath containing $5 \times 10^{-7}M$ STA and subsequently annealed (300°C , 1 h) in N_2 atmosphere. The grain sizes obtained are also included in Table I. From the values of grain sizes, it is clear that largest grains are only achievable, when the films are prepared with STA and subsequently annealed in N_2 atmosphere.

Resistivity and Hall effect measurements were made at room temperature. Thermoelectric power measurements showed that the films are n-type. The resistivities, carrier concentrations, and mobilities of the different films are given in Table I.

Figure 2 shows the optical absorption $(\alpha h\nu)^{1/2}$ vs. incident photon energy ($h\nu$) curves for Sb_2S_3 films with (Fig. 2a) and without (Fig. 2b) STA incorporated annealed in N_2 atmosphere. The plots are found to be linear, suggesting that the bandgaps of the Sb_2S_3 films are indirect in nature. Extrapolation of these curves to zero absorption coefficient gives the optical energy gap of the Sb_2S_3 films, which are 1.85 eV for the as-deposited unannealed (Fig. 2c) and 1.74 eV for the annealed sample. The decrease in E_g after heat treatment may be due to increase in effective grain size and in the closer stoichiometric composition on annealing. The later value of E_g agrees closely with the value of 1.77 eV for polycrystalline Sb_2S_3 films (17).

The solar cell characteristics of the annealed sample with and without STA was evaluated at a constant illumination intensity of $40 \text{ mW}/\text{cm}^2$ and is shown in Fig. 3. The as-deposited Sb_2S_3 film without STA showed poor I-V characteristic (Fig. 3). But after annealing the films (300°C in N_2 atmosphere) the I-V properties improved significantly (Fig. 3b). This is mainly due to the influences of annealing of the films causing a significant in-

crease in the effective grain sizes (cf, Table I) and a decrease in grain boundary area due to migration of smaller crystallites, and the joining of similarly oriented grains to form bigger crystallites. The decrease of effective grain boundary area decreases grain boundary scattering, surface scattering, and space charge scattering resulting much improved I-V characteristics. But STA incorporated and subsequent annealing in N_2 atmosphere, the Sb_2S_3 film showed the best I-V (Fig. 3c) characteristics with open-circuit voltage (V_{oc}) 540 mV, short-circuit photocurrent density (J_{sc}) $5.6 \text{ mA}/\text{cm}^2$, fill factor of 0.52 and cell efficiencies 3.9%, respectively. The significant improvement of the qualities of the films and the properties of PEC solar cells may be due to the influence of the STA ($\text{SiW}_{12}\text{O}_{40}^{4-}$) used in the deposition bath. It has already been established [(12-15, 18, 19) and the references therein] that the modification of semiconductor surfaces with STA (12) and electrodeposition of metal with STA (14, 15, 18, 19) can produce good electrocatalytic interfaces for the PEC and for the hydrogen evolution reaction (HER), respectively. The improvement of the PEC characteristics and the qualities of the Sb_2S_3 films deposited with STA may also be attributed to the induction of a favorable energy state within the bandgap favoring the charge-transfer kinetics at the electrode interface (20). The mechanism of the electrocatalytic activity of the STA on the improvement of the Sb_2S_3 thin film properties and the PEC cell characteristics is not well understood and is the subject of current investigations. However, this communication demonstrates the feasibility of preparing semiconductor grade n- Sb_2S_3 thin films by an inexpensive chemical deposition route and the possibility of achieving photoactive electrode material for photovoltaic or PEC solar cells.

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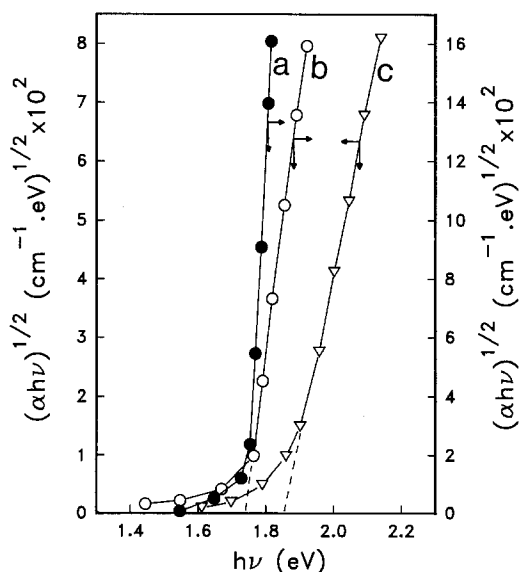


Fig. 2. Variation of $(\alpha h\nu)^{1/2}$ vs. $(h\nu)$ plot: (a) Sb_2S_3 film prepared with $5 \times 10^{-7}M$ STA and annealed at 300°C for 1 h in N_2 atmosphere, (b) same as (a) but without STA; and (c) as deposited film without STA. The optical absorption coefficient, α , is in cm^{-1} .

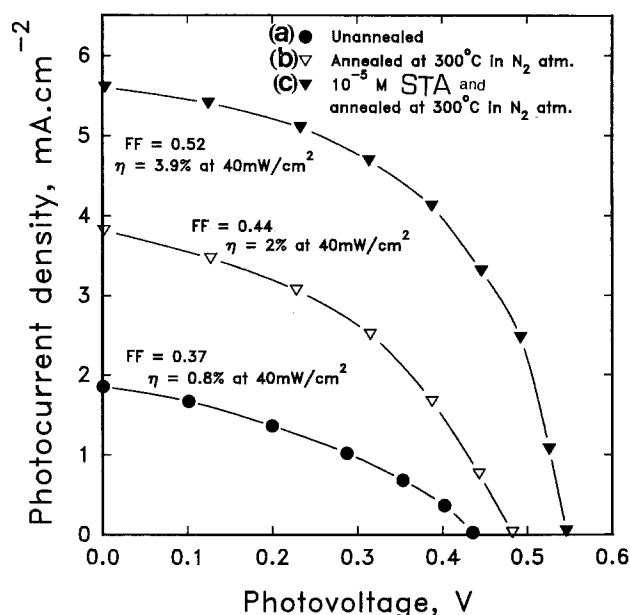


Fig. 3. The current (I)-voltage (V) characteristics of the n- $\text{Sb}_2\text{S}_3/0.01M$ KI/C PEC cell, (a) as-deposited n- Sb_2S_3 film electrode without STA; (b) same as (a) but annealed at 300°C in N_2 atmosphere for 1 h and (c) $5 \times 10^{-7}M$ STA incorporated Sb_2S_3 electrode and annealed at 300°C in N_2 atmosphere for 1 h.

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